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Photoinduced phase-matched second-harmonic generation in azodye-doped polymer films

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Phase-matched second-harmonic generation (SHG) in azodye-doped polymethylmethacrylate films was demonstrated using the nonresonant optical poling technique. During the seeding process, samples were irradiated simultaneously by coherent superposition of the fundamental and the second-harmonic light of a femtosecond laser. Optical poling experiments were performed at three wavelengths of 1500, 1320, and 1300 nm, respectively. The quadratic dependence of SHG on the film thickness showed that a $\chi^{(2)}$ grating that satisfied the phase-matching condition for SHG was optically induced in the polymer films. The SHG conversion efficiency of a 105 μm thick film was estimated to be about 2%. A relaxation retardation effect of the photoinduced $\chi^{(2)}$ was also observed in the thick films. © 2001 American Institute of Physics. [DOI: 10.1063/1.1343890]

I. INTRODUCTION

Second-order nonlinear optical (NLO) polymers are very attractive for applications in optical communications and in high-density optical data storage.^{1,2} Poling techniques are usually used to realize the second-order NLO function of the polymer films. There are three kinds of poling techniques available at present, thermal-assisted electric-field poling,³ photoassisted electric-field poling,⁴ and all-optical poling.⁵ All-optical poling has been demonstrated in azoaromatic acrylic copolymers using a dual frequency laser.⁵⁻⁷ The physical mechanism of the effect consists of two processes: orientational hole burning and reorientation of azodye molecules.^{6,8} Under the excitation of a fundamental light along with its second-harmonic light, orientational hole burning of azodye molecules occurs through the interference of two-photon absorption at the fundamental frequency and one-photon absorption at the doubling frequency. Orientational hole burning is followed by reverse *trans-cis-trans*-isomerization, which finally leads to a net permanent polar orientation of molecules. This technique possesses some of the following advantages: phase matching for second-harmonic generation (SHG) can automatically be achieved, no electrodes are required, and micropatterning of the second-order susceptibility can be simply achieved by scanning the focal area over the sample surface.

There were, however, two problems to overcome for the application of this poling technique to photonic devices: one was the relaxation of the induced polar orientation of azodye molecules, and the other was low SHG conversion efficiency. In order to solve the former, we presented a thermal-

assisted optical poling, and successfully achieved thermosetting enhancement of the induced polar orientation stability in polymer films and glasses.^{9,10} In a resonant optical excitation process, it appears to be difficult for the SHG conversion efficiency to benefit from phase matching achieved automatically in large propagation distances due to the absorption of samples. Recently, we reported all-optical poling of azodye-doped polymethylmethacrylate (PMMA) films using the 1500 nm fundamental and 750 nm second-harmonic light of a femtosecond laser.¹¹ Although the SHG conversion efficiency still was low due to the use of thin films only several micrometers thick, the nonresonant excitation should permit the use of larger film thickness, which should in turn result in a significant increase of the conversion efficiency. In this article, we experimentally demonstrate phase-matched SHG in thick films using the nonresonant optical-poling technique. Optical poling was performed at three different conditions in which wavelengths of two seed light beams were set, respectively, at 1500 and 750, 1320 and 660, and 1300 and 650 nm. A quadratic dependence of SHG on the film thickness and a relaxation retardation effect of the photoinduced $\chi^{(2)}$ were observed in the films.

II. EXPERIMENTS

A. Samples

The samples used in this study were prepared by dissolving to a 15% mass ratio purified disperse red 1 (DR1) and medium molecular weight PMMA in tetrahydrofuran. The films were spin deposited onto glass substrates, and dried for several hours at 160 °C. Films with different thicknesses were prepared by adjusting the viscosity of the solution and the revolutions per minute of the spin coater. The absorption

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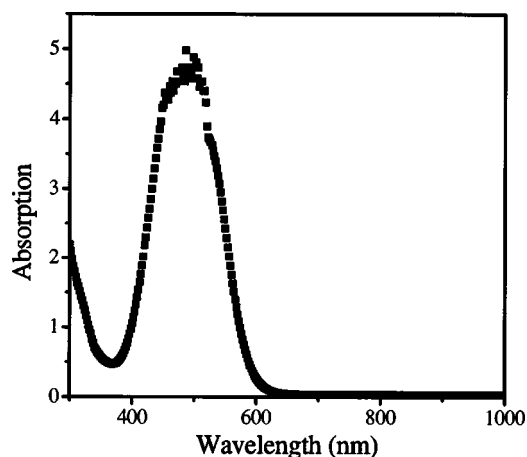


FIG. 1. Absorption spectrum of an azodye-doped PMMA film.

spectrum of a 1.3 μm thick film is shown in Fig. 1, from which one can see that the absorption band peaks at 480 nm, and the film is almost transparent at wavelengths larger than 650 nm.

B. Experimental setup

A Ti:sapphire laser system with an optical parametric amplifier (OPA) which emitted 150 fs laser pulses at a repetition rate of 1 kHz was used for all-optical poling of the films, and the wavelength of the light from the OPA could be tuned from 300 to 3000 nm. The average power of the laser was about 50 mW at wavelengths ranging from 1300 to 1500 nm. A seed beam ω for all-optical poling was split from the source beam and passed through a time-delay device and a $\lambda/2$ plate to control the path length and the polarization of the beam, respectively. Another beam separate from the source beam was frequency doubled by a KDP crystal, which served as another seed beam, and is denoted seed beam 2ω here. The two collinear seed beams were introduced into the film sample through a 6 cm focal-length quartz lens. We achieved time superposition of pulses between the two seed beams by adjusting the time-delay device and observing the optical Kerr effect of CS_2 . During the optical-poling process, the two seed beams were introduced simultaneously into the film sample; during the probe, beam 2ω was blocked by a shutter and only beam ω remained incident. The SHG signals of beam ω were detected by a photomultiplier and observed and averaged by an oscilloscope. Beam ω passing through the sample was blocked by a heat-absorbing filter placed behind the sample, and allowed only the SHG signal to pass through it. Typical fluences of the two seed beams at the sample were approximately 1.5 mJ/cm^2 for beam ω and 0.03 mJ/cm^2 for beam 2ω , respectively.

III. RESULTS AND DISCUSSION

A. Dependence of SHG on film thickness

By adjusting the delay device, we measured the dependence of photoinduced SHG on the temporal correlation of the two seed beams, and observed that all-optical poling of the films could be performed only when the two seed

beams were coherently superpositioned. This indicated that all-optical poling resulted from coherent excitation of the two seed lights for azodye molecules in the films. To confirm that the SHG signals were from phase-matched SHG, we measured the dependence of the SHG signal intensity versus the sample thickness. Figure 2(a) shows the results measured for the films written by two seed beams with wavelengths of 1500 and 750 nm, where all of the measurements were made after the photoinduced $\chi^{(2)}$ of the films increased to their saturation values. It can be seen from Fig. 2 that the SHG signals increase proportionally to the square of the film thickness. It is well known that for a thick film of thickness of larger than SHG coherent length (the coherent length of these films is about 12.5 μm), the quadratic thickness dependence of the SHG intensity occurs only in the phase-matched condition. A peak conversion efficiency of 2% was observed for the 105 μm film and a fundamental light intensity of 9 GW/cm^2 incident on the film. Obviously, this high conversion efficiency benefited from phase-matched SHG in the thick film. We also observed that the SHG intensity of the films departed from the quadratic length dependence when the thickness of the films was larger than 105 μm . This probably is due to the group velocity mismatch between seed beam ω and seed beam 2ω . The group velocity mismatch causes the ω seed pulse to displace against the 2ω seed pulse as they propagate along in the film. This reduces the effective interaction length and decreases the optical-poling efficiency.

Moreover, results similar to those described above were also observed when the wavelengths of the two seed beams were set, respectively, at 1300 and 650 and 1320 and 660 nm. The experimental results for both cases are shown in Figs. 2(b) and 2(c), respectively.

B. Dependence of the relaxation of the photoinduced $\chi^{(2)}$ on film thickness

As reported by us in a previous study,¹¹ photoinduced $\chi^{(2)}$ of DR1-doped PMMA films had obvious relaxation. We found here, however, that the relaxation rate decreased with increasing thickness of the films, and when the SHG signal intensity from the thick films reached a certain level, the relaxation of the photoinduced $\chi^{(2)}$ was completely suppressed. Figure 3 shows the typical relaxation measured for the three films with thicknesses of 105, 40.5, and 8.2 μm . The films were written by the 1500 and 750 nm seed beams. All of the measurements were made after the photoinduced $\chi^{(2)}$ of the films increased to their saturation values. It can be found from Fig. 3 that for the 105 μm film no measurable change in the SHG signals occurred over a period of 30 min. And the SHG signal intensity of the film was also observed to be comparable with the 2ω seed intensity.

The relaxation retardation effect of the photoinduced $\chi^{(2)}$ for the 105 μm film is probably related to the seeding for the film by the ω readout light and the SHG signal light (we call it “self-seeding” here). In case of the 105 μm film, this self-seeding could counteract the relaxation effect during the readout process because the SHG signal light of the film was strong enough to completely suppress the relaxation of

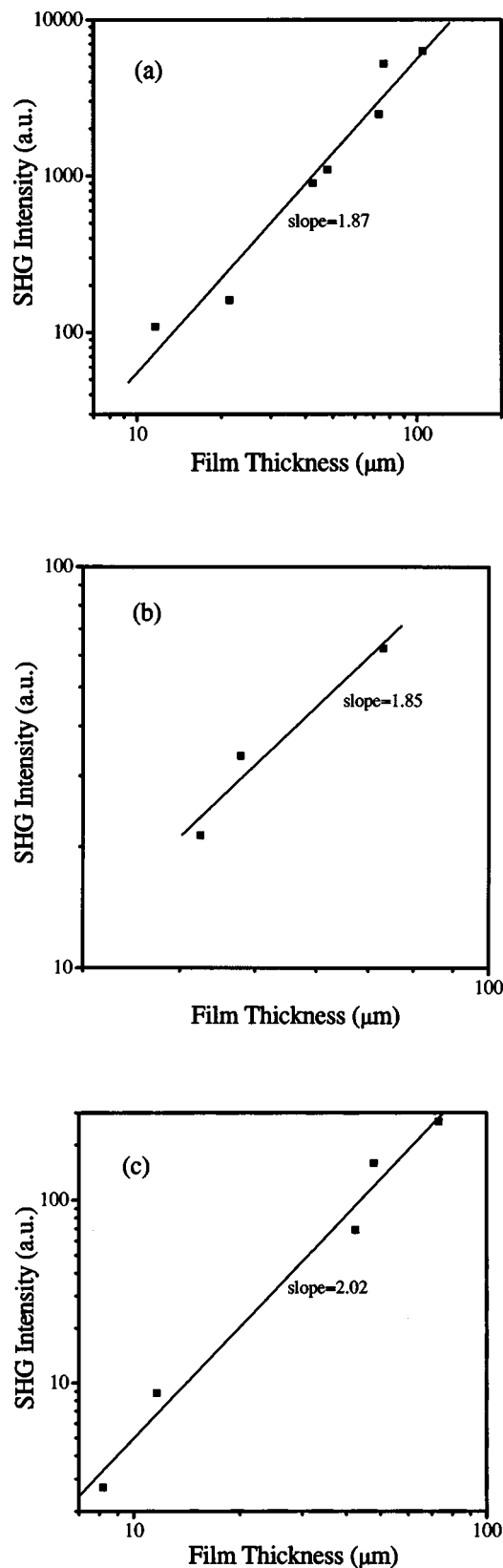


FIG. 2. Log-log plots with a linear fit of a slope near 2, displaying SHG intensity dependence on the film thickness squared. In the optical-poling processes wavelengths of the ω and 2ω seed beams were set at, respectively, 1500 and 750 (a), 1320 and 660 (b), and 1300 and 650 nm (c).

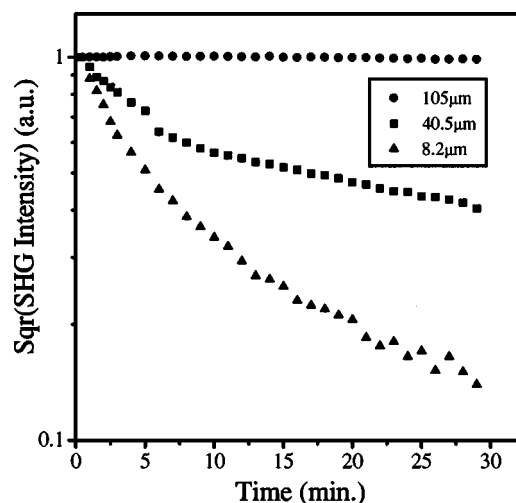


FIG. 3. Relaxations of the photoinduced $\chi^{(2)}$ of three films with different thicknesses. The films were written optically by two seed beams with wavelengths of 1500 and 750 nm.

the photoinduced $\chi^{(2)}$. In contrast, for the two films with thicknesses of 40.5 and 8.2 μm , the SHG signal intensities of the films were too low to completely suppress the relaxation.

C. Tensor analysis of the photoinduced $\chi^{(2)}$

For tensor analysis, we performed experiments to measure the x and the y components of the SHG signals by keeping the back polarizer fixed in the vertical (x) or horizontal (y) position and rotating the readout-beam polarization. Figure 4 displays the tensor curve for the x component for a 73 μm film written by the 1300 and 650 nm seed beams. The tensor curve was fitted by general polarization expressions as the following:¹²

$$|E_x^{2\omega}|^2 \propto |\chi_{xxx}^{(2)} \cos^2 \theta + 2\chi_{xxy}^{(2)} \cos \theta \sin \theta + \chi_{xyy}^{(2)} \sin^2 \theta|^2,$$

$$|E_y^{2\omega}|^2 \propto |\chi_{yyy}^{(2)} \sin^2 \theta + 2\chi_{yyx}^{(2)} \cos \theta \sin \theta + \chi_{yxx}^{(2)} \cos^2 \theta|^2,$$

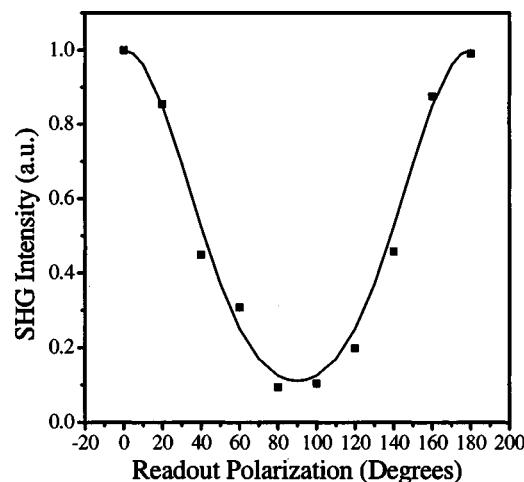


FIG. 4. Tensor data and fits for the x component of SHG signals from the photoinduced $\chi^{(2)}$ of the 73 μm film. The films were written optically by two seed beams with wavelengths of 1300 and 650 nm.

where θ is the readout beam polarization measured with respect to the vertical x axis. The best fits gave

$$\chi_{xxx}^{(2)}/\chi_{xyy}^{(2)} \approx 3,$$

and

$$\chi_{xxy}^{(2)} = 0.$$

From the measurements for the y component, we obtained

$$\chi_{xxx}^{(2)}/\chi_{yyy}^{(2)} > 12,$$

and

$$\chi_{yyx}^{(2)} = 0.$$

The results of this tensor analysis indicate that for collinearly polarized seed beams the photoinduced $\chi^{(2)}$ in the film exhibited axial symmetry along the seed beam polarization direction.

Here, we could not measure the magnitudes of the photoinduced $\chi^{(2)}$ of the films with femtosecond pulses because of the limit of our experimental conditions. To show the capability of optical poling for the films using a nonresonant femtosecond laser, we measured the SHG intensity ratio for the 73 μm film, I_s/I_q , where I_s and I_q are, respectively, the SHG intensities of the film and a Y-cut quartz for the same readout wavelength and readout power. During the seeding processes, wavelengths of two seed beams were set at, respectively, 1300 and 650, 1320 and 660, and 1500 and 750 nm. The square root of the SHG intensity ratio between the film and the quartz, $(I_s/I_q)^{1/2}$, was measured to be 6.6, 7.5, 18.6, respectively, for fundamental wavelengths of 1300, 1320, and 1500 nm. These values are near to that of optical poling made using a resonant nanosecond laser,⁹ indicating effective optical poling also can be achieved even in non-

resonant excitation when a femtosecond laser with high peak power is used.

IV. CONCLUSION

We experimentally demonstrated phase-matched SHG in azodye-doped PMMA films using the nonresonant optical-poling technique. Experiments were performed at three wavelengths, 1500, 1320, and 1300 nm. Square dependence of SHG on the film thickness was observed, and the SHG conversion efficiency of the 105 μm film was estimated to be about 2%. The relaxation retardation effect of the photoinduced $\chi^{(2)}$ also was observed as the film thickness was increased. It is expected that this study will promote the application of all-optical poling in photonic devices.

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